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Oxidative Coupling of Methane over BaO Mixed with CaO and MgO

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Various metal oxides mixed with BaO were studied as a catalyst for coupling of methane. For example, a BaO-CaO catalyst shows a high activity (20.9 mmol $h^{-1}g^{-1}$) for the C_2 formation (C_2H_6+C_2H_4) with a high C_2 selectivity(61.1%) under the following conditions; 1073 K, $P(CH_4)$ = 40 kPa, a ratio of CH_4 to O_2 = 5.0, and W/F = 3.39 g h mol^{-1}.

Alkali doped catalysts (Li-MgO,[1] Li-Sm_2O_3,[2] and Na-MgO[3]) have been reported to show the highest yield of C_2 hydrocarbons (C_2H_6 and C_2H_4) among the various catalysts[1-9] for the title reaction. In addition, also BaO and $BaCO_3$[9] have been found to show a high C_2 yield being comparable to the alkali doped catalysts. We have found the mixing effect of alkali metal earth oxide containing BaO on the isomerization and the dehydrogenation of 1-butene.[10] Here, we report the catalytic activity of various mixed oxides containing BaO for the title reaction.

The catalysts used here were prepared by soaking various metal hydroxides in an aqueous $Ba(OH)_2$ solution, followed by drying in air at 393 K for 24 h. The BaO content was 10±1 wt%. The sample(0.5g and 32-60 mesh) was activated at 873 K in a flow of O_2 diluted with He gas for 1-2 h. The reaction was carried out in a conventional flow reactor at atmospheric pressure. The reaction conditions were as following, T= 873-1103 K, $P(CH_4)$= 40 kPa, $P(CH_4)/P(O_2)$= 5.0, and W/F= 3.39-13.6 g h mol^{-1}. The all reaction products were analyzed by gas chromatography.

The most catalysts gave the best yield or selectivity for the C_2 formation around 1073 K. Table 1 shows the results of the reaction at 1073 K for the catalysts containing BaO. The yield and the selectivity were calculated on the basis of conversion of methane to the each product. As is shown in this table, the BaO-MgO and BaO-CaO are much more effective for the reaction than the other catalysts prepared by mixing BaO with acidic or amphoteric oxides. Such a prominent supporting effect of basic oxide has been found also for the PbO supported catalysts[7] in the oxidative coupling of methane.

The BaO-MgO and BaO-CaO have been found to give remarkably higher C_2 selectivity and C_2 yield than MgO, CaO, and BaO. The commercial BaO showed a low catalytic activity, probably due to the low specific surface area of the BaO powder(<1 m^2/g). For the BaO-CaO catalysts, the C_2 yield was little affected by increasing

Table 1. The Catalytic Activity for Oxidative Coupling of Methane at 1073 K[a)]

Catalyst	Conversion/%		Selectivity/%		C_2 Yield/%	S.A.[b)]
	CH_4	O_2	C_2	C_2H_4		m^2/g
BaO - SiO_2	10.9	60.8	24.7	12.4	2.7	57
- TiO_2	15.2	99.8	4.3	1.7	0.7	38
- ZrO_2	14.5	99.7	14.7	6.5	2.1	2
- Al_2O_3	16.4	99.1	12.1	7.6	2.0	135
- Fe_2O_3	13.0	98.0	3.5	0.0	0.5	32
- MgO	23.0	99.3	56.7	32.3	13.0	18
- CaO	21.5	99.7	57.1	30.3	12.3	12 (7.7)
5wt% BaO-CaO	20.5	99.7	59.4	33.3	12.3	11 (9.8)
20wt% BaO-CaO	21.6	99.8	57.2	33.2	12.4	(4.4)
30wt% BaO-CaO	20.5	99.7	61.3	34.9	12.3	(2.5)
(20wt% BaO-CaO[c)]	23.2	99.8	61.1	33.6	14.2	)
MgO	17.0	98.5	30.5	19.5	5.2	60
CaO	18.8	99.7	46.8	25.7	8.8	42 (11.0)
BaO (Merck)	9.4	32.9	45.7	23.3	4.3	(< 1)

a) W/F = 13.6 g h mol^{-1}. b) The BET surface area before (after) the reaction.
c) W/F = 3.39 g h mol^{-1}.

BaO content. Nevertheless, the surface area decreased almost linearly from 0 to 30 wt% with the increase of BaO content. These facts suggest that the mixing effect of BaO on the C_2 formation was not simply due to the variation in the surface area of the catalysts.

A maximum C_2 yield of 14.2% was obtained with a high C_2 selectivity (61.1%) at 1073 K and W/F of 3.39 g h mol^{-1} over the 20 wt% BaO catalyst. From these results space time yield of C_2 compounds was calculated to be 20.9 mmol $h^{-1}g^{-1}$, which was higher than those obtained for the coupling of methane over $LaAlO_3$[7)] (8.31 mmol $h^{-1}g^{-1}$, 983 K), and PbO/MgO[8)] (11.1 mmol $h^{-1}g^{-1}$, 1023 K).

XRD analysis suggested that the formation of some mixed compounds, probably the mixed oxides or the mixed carbonates, together with $BaCO_3$. However, further studies are required to clarify about the relation between the catalytic activity and the formation of such as mixed oxides and carbonates.

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